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II. Thermodynamics of Fourier-like radiative conduction heat currents, and equilibrium temperature gradients*

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Abstract : A thermodynamic basis is provided for previous experimental results [*Indian J. Phys.* **71B** 661 (1997)] It is shown that the temperature power law of the emitted radiation is dependent on the geometry and dimensionality of the system from which the radiation issues A two dimensional flat surface of charged oscillators will emit radiation that predominantly varies linearly with temperature, whereas a pinhole on a three-dimensional structure made up of sheets of surface charged oscillators will emit the usual T^4 dependent (Stefan-Boltzmann) radiation. Hitherto, applications in radiative heat transfer have used the T^4 form regardless of system dimensionality An expression for heat radiation for systems of varying dimensionality, is provided The consequences of dissimilar equilibrium temperature between the surface oscillators of a blackbody and objects suspended in the cavity of a blackbody are developed classically to yield generalized criteria for equilibrium in these cases where Newton's law of momentum conservation does not obtain It is indicated that the Zeroth law is inferred from the Newton's Laws of momentum. Analogues of the Boltzmann's constant under the breakdown of the Zeroth Law, and an extended Second Law formulation are rigorously developed requiring coupling coefficients where no contradiction to Kelvin's Second Law Principle is found Kirchhoff's Heat Radiation Law, the Fourier Heat Conduction Law and the Fourier Inequality are all generalized This concluding sequel is a detailed development of the brief experimental and theoretical results presented elsewhere [*1993 National Physics Conference Proceedings, Malaysia Institute of Physics*, p 267 (1994)]

Keywords : Fourier-like radiative heat transfer, equilibrium criteria, breakdown of Zeroth Law and Second Law, generalised Fourier, Kirchhoff and Second Law

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1. Introduction

The experiments in the first sequel require theoretical reconciliations between the classical and quantum developments [1, 2]. The work here is an extension of a study relating classical

*This sequel is dedicated to the memory of author's Father Donald Jeyasingam Jesudason.

statistical mechanics to Quantum theory *via* the fundamental Planck black body (bb) spectral formula [1]. In that study, an entirely classical derivation of the Planck result was obtained by considering the charged oscillators on the surface of the bb cavity as being represented by a damped oscillator equation without external force (because the relaxation time τ is considered short enough) written as*

$$m\ddot{x} + a\dot{X} + kX = 0, \tag{1}$$

where $a = m\bar{\gamma}$ is the combined electromagnetic and viscosity damping term. For N scattering centres, the total radiation scattered $\delta R(\omega)$ in time τ is given [1] by

$$\delta R(\omega) = a < X_0^2 > N.4\pi^2 v^2 \tau.\, p(E)d\ddot{E} / 2 \tag{2a}$$

$$= 8\Omega v^3 \alpha\pi^2 p(v)dv.\tau$$

for the frequency range $\omega - \delta\omega / 2 \le \omega \le \omega + \delta\omega / 2$, where $\omega = 2\pi v$ and

$\Omega = a < X_0^2 > N4\pi^2 / 2$. The total energy received or scattered over time τ per frequency mode v is therefore

$$\delta r(\omega) = \delta R(\omega) / D(v)dv. \tag{2b}$$

When approximations are made concerning the probability distribution function $p(E)$, then we write $\varepsilon = hv = \delta r(\omega)$, where an analysis based on generalized equipartition [1] yields the Planck constant h for the oriented scattering of N centres as

$$h = 4c^3 \alpha\pi^3 N\tau^2, \tag{2c}$$

where $\alpha = m\left\langle X_0^2 \right\rangle / 2$, and also [1]

$$\langle\langle P\rangle\rangle = k'T\gamma. \tag{3}$$

In eq. (2c), the average energy ε emitted at frequency v over relaxation time τ is $\varepsilon = hv$, which is the original Planck hypothesis regarding emission of radiation in his bb studies, whereas eq. (3) gives the *total* emission per oscillator by double averaging over all frequencies and amplitudes; by the equipartition theorem, eq. (3) is a thermal radiation law for a two-dimensional surface, surrounding a cavity for constant γ. Eq. (3) holds for one-dimensional random oscillator as well. Further considerations in equipartition allow the Planck spectral expression to be derived from eq. (2c), as well as predictions to be made concerning the photoelectric effect and multi-photon processes [1]. These developments lead to some consequences outlined below which refer to ideal models [1] requiring moderation by terms due to interference in experimental determinations. In this work, deliberately simplified Euclidean coordinates which can easily be generalized to systems of a different metric, such as in gravitation theory, are used; structure and axiomatics derived from experimental and other considerations are emphasized from which a suitable topology may be selected for applications where this Euclidean metric is not suitable. The following ideal (and therefore approximate) results are anticipated for systems using Euclidean coordinates. All temperatures of systems are determined by mechanically coupling them to a body whose temperature is known, assuming that the Zeroth Law holds with Newtonian conservation of momentum for the particles in and on the surface of the body.

*Nomenclature of all terms are given in Appendix

2. Some Theoretical consequences

2.1. Pure bb emissions from a cavity with variable index of refraction :

The index of refraction is always frequency (ν)-dependent if dispersion [3] is considered, so that we may write the index as $n = n(\nu)$. We may therefore, consider statistical scattering of energy by the surface oscillators over every element $d\nu$ of frequency ν in a standardized bb cavity of unit volume having N oscillators, a mean relaxation time τ, where $\alpha = m < X_0^2 > /2$, and where $m, < X_0^2 >$ and c are respectively the mass, mean square amplitude of the oscillation, and the velocity of light in vacuum respectively [1]. Since the elementary quantum $\varepsilon = \delta r(\omega)$ is, from (2b), dependent on $D(\nu)$, then if the index of refraction of the 3-dimensional bb cavity is $n = n(\nu)$, we expect a modification to the radiancy from such a bb. $D(\nu) = 8\pi\nu^2 c_m^{-3}$, where c_m is the velocity of light in the medium of refractive index $n(\nu) = c/c_m$, and $\lambda_m \nu = c_m$ where λ_m is the associated wavelength; ν does not change when light travels through two media with different n's, such as in the case of the bb between the surface oscillators and the bb cavity. From the definitions, $D(\nu) = 8\pi\nu^2 c^{-3} n^{-3}$, and from (2a) and (2b), ε must transform as $\varepsilon = \delta r(\omega) = \varepsilon' = h\nu n^{-3}$.

Since $\bar{E}(\nu) = \bar{\varepsilon}(\nu) = \sum_n n\varepsilon(\nu)p(\varepsilon(\nu)n)$

$\mathrm{Lim}\ M \to \infty$

where

$$p(n\varepsilon(\nu)) = \exp[-n\varepsilon(\nu)/kT] \Big/ \sum^{\infty} \exp[-m\varepsilon(\nu)/k'T]$$

we derive

$\bar{E}(\nu) = \varepsilon(\nu)/(\exp(\varepsilon(\nu)/k'T) - 1)$. The Planck energy density is $U_\nu = D(\nu)E(\nu)$, which therefore modifies to $U'_\nu = 8\pi\nu^3 hc^{-3}/[\exp(h\nu/n^3 k'T) - 1]$. The radiancy is

$$E_{b\nu} = \frac{c_m U'_\nu}{4} = \frac{cU'_\nu}{4n} = (2\pi h\nu^3/nc^2)[\exp(h\nu/n^3 k'T) - 1]^{-1} \tag{4}$$

On the other hand, the standard result is [4]

$$E_{b\nu} = (2\pi h\nu^3 n^2/c^2)[\exp(h\nu/kT) - 1]^{-1}$$

However, Wiebert [5] has pointed out that this result is hardly ever used. From the above, we see that the Planck density derives from the canonical distribution function applied to the wave modes within the 3-dimensional cavity, whereas the $\gamma k'T$ energy emission or absorption term derives from applying a canonical probability function for oscillators with one or two degrees of freedom. Hence, the dimensionality of the system is crucial to the energy density of radiation emitted by the system. The role of dimensionality has been neglected in normal heat transfer applications, where the 3-dimensional Planckian form is routinely assumed to hold for 2-dimensional surfaces [4,5].

2.2 Explainations for the results of active and passive heating experiments of previous sequel [2].

The first order results from the theory presented in ref. [1] indicate two separate effects, the first being the presence of a finite leakage or radiative emission current $\gamma k'T$ (γ being the electromagnetic-mechanical viscosity) per oscillator for each degree of freedom on the 2-dimensional surface. This result should be compared to the emission density expression $I(\omega)$ provided by Feynman et al [6] for the same dimensionality, written as $I(\omega) = \omega^2 kT / \pi^2 c^2$ where the integral of $I(\omega)$ with respect to ω, the frequency, is not finite for a surface. His conclusion then is that there is something wrong with the classical equipartition since infinities are involved, in contradiction to experiment. However, here we have shown that no infinities are involved if the appropriate probability distribution function and the dimensionality of the system are taken into consideration. The second effect is the 3-dimensional build-up of electromagnetic energy in a cavity fulfilling the boundary conditions (such as a perfectly reflecting surfaces up to relaxation time τ for the system of oscillators lining the cavity [1]) where strict equipartition may be applied to each different Hamiltonian system comprising the stationary vibrational modes to yield the average bb energy density u_o ; a punctured cavity would cause an energy stream (in vacuo) $u_o c/4$ (unit area and time) which is not connected directly with the leakage current $\gamma k'T$ emitted from a (2-dimensional) surface, and thus the detailed balance reasoning which connects directly and equally the 3 and 2-dimensional energy dissipation vectors in the standard treatments call for some further clarification since it is open to question both theoretically and experimentally [4,5]. We argue here that the larger linear transport of thermal radiation reported in the previous sequel for foils wrapped about a non-conducting heater, is due to this $\gamma k'T$ term.

Within the context of bb radiation with internal surface S having charge density n'', [1], we preserve the traditional gross relations between emission P_e ($= n''\gamma k'T +$.... higher order terms in T) and incidence power $P_i(T)$ (defined as that power due to the bb cavity relative to the material composition of the surface of the cavity at temperature T with incident flux $u_o c/4$) [7] by defining

$$a(T') = P_e(T')/P_i(T), \tag{5}$$

where $a(T'')$ is the absorptivity of a substance suspended in the cavity relative to the conditions that must be specified as a standard state (such as $P_i(T)$ having a standard value by appropriate adjustment of the geometric cavity parameters) and T' its temperature. If $P_i(T)$ is specified, then $a_j(T_j')/P_{ej}(T_j')$ is a function of T only, the temperature of the standard cavity for all substances j, where T_j' is the temperature of the object in the thermal field. The above definition is required for the generalization of the Kirchhoff Law; previously, it was always assumed that the incident radiation at least had bb radiation [7] intensity. In accordance with convention and standard usage, this assumption is embedded in the above definition.

From the above considerations of the difference between surface and bb emission, we can couple the two effects for a general surface by writing the general total surface thermal radiation (radiathermal) emission P_g as

$$P_g(g,T) = \Pi(g,T)\sigma_s T^4 + \sum_i l_i(T,g)T^i + A(g,T)\sigma_s T^4, \tag{6}$$

where the summation terms are for the surface oscillator leakage current in powers of T $= n''k'\gamma T$ for first order estimate), $A(g, T)$ is an average coefficient due to the possible build-up of bb radiation due to the surface having some three dimensional characteristics due to inhomogeneities (such as microcavities that may cause a partial build-up of bb cavity radiation which is then subsequently emitted), Π is a new thermal bb permeability factor determining the leakage of the bb-type radiation of the lattice that builds up as a result of the apparent excess charge density of the surface which scatters into the 3-dimensional lattice [8–9], as well as the internal scattering of the radiation generated by the oscillators within the cavity; this bb heat then permeates through the two dimensional outer surface of the sysem. The quantum concept of surface charge arises from the Fermi level surface [9], whereas classically, one can evoke the construction of Poisson's equivalent distribution for materials with dielectric properties, where for a point P' outside the dielectric, the potential is the same as that due to a volume distribution of density $\rho_p = -\,\mathrm{div}\,\boldsymbol{P}$ and a surface distribution of density $\sigma_p = \boldsymbol{P}.\boldsymbol{n}$, the normal component of $\boldsymbol{P}$, the polarization [9]. This dielectric simulation may be applied to a metallic conductor where there exists a separation of charge due to the mobile valence electrons, causing an instantaneous dipole for each atomic center. Eq. (6) is not compatible with directly equating the bb component with a linear or other power law in temperature. In conducting media, there is an attenuation of the e.m. waves created at the surface [10]. For a complex refractive index $\hat{\mathbf{n}} = n + ik$, the freely propagating wave $\boldsymbol{E} = \boldsymbol{E}'\exp[-i(\omega t - \boldsymbol{u}.\boldsymbol{r}.n/c)]$ becomes $\boldsymbol{E} = \boldsymbol{E}'[\exp(-k\zeta/c)].\exp[-i\omega(t - n\boldsymbol{u}.\boldsymbol{r}/c)]$ with the attenuation factor ζ which is a linear function of propagation distance. However, subject to the boundary conditions used to derive the bb radiation [1], each mode is independent with its own partition function D_i, so that a Planck-type distribution will still ensue with a T^4 density, but the parameters such as the Stefan constant would differ from a vacuum cavity since it would be a function of the internal variables such as the conductivity, permittivity *etc* ; $\boldsymbol{g}$ pertains to all such internal variables including geometry The permeability factor accounts for the changes of the partition functions due to attenuation (of the standing wave patterns) and the penetration of the waves through the surface layer with its charge density. The geometrical factors $\boldsymbol{g}$ include structure (such as a coiled sheet that can create standing wave patterns at the interstices of succeeding sheets in the coil, or a solid such as a cylinder where the standing wave pattern is found within it for the common relaxation time τ[11]). Other factors in $\boldsymbol{g}$ include electric currents which may contain the modes along the surface (such as a heating coil). The Einstein treatment of the specific heats of solids with the quantized oscillators may be viewed as another mode of absorption from the modes ***within*** the solid which has mean energy $\varepsilon = h\nu$ [1] injected in per mode with average relaxation time τ. The average time τ in which increments of energy $h\nu$ may be absorbed by the atomic oscillators by virtue of the e.m. modes that exists within the solid, determines whether a process is quantized or not [11]. Quantization is said to occur when τ is very small ($\to 0$) ; σ_s is the Stefan constant used to normalize eq. (6).

2.3. Temperature gradients, equilibria and Kirchoff's laws :

Zon [12] has derived expressions in which the bb temperature T_p and the Maxwellian temperature T_M are related according to $T_M = T_p(1 + 2\pi\alpha' T_p / 9mc^2)$, $\alpha' = e^2 2\pi / hc$, m being the mass of the electrons. Since our derivation [1] connects a common relaxation time τ with a fixed temperature T which is the same for both electrons and bb radiation, the acceptance of both theories suggests the possibility of minute temperature differences between the bodies since if $T_p = T_c$, (where T_c is the common temperature of the resonators in the boundary matrix (bm) or surface that causes the cavity radiation), then a body of N electrons bathed in this field will have a temperature $T_M \neq T_p = T_c$ in general. Since T_M is understood to be a Maxwellian temperature, neutral uncharged Newtonian particles at low densities bathed in this bb radiation must also have a temperature T_p. Thus from the quantum-mechanical assumptions, it seems possible to couple a composite system in the steady state which exhibits temperature differences. If T_p is relative to another temperature scale, then Zon's equations are superfluous, and no new information is provided in his derivations. Thus, it is of interest to derive generalizations to the Zeroth Law from a more traditional approach based on the experimental definition of what constitutes the equality of temperature between two bodies; further the experiments in the previous sequel are supportive of this suggestion, but the order of magnitude of the effect measured is way beyond that predicted by quantum theory. A reconciliation may be aided by noting that the definition of equal temperature by material (*i.e.* mechanical) contact between two bodies with zero *net momentum* (and therefore energy) flow across the boundary of the two systems, involves corpuscles obeying Newtonian dynamics, whereas Planck for instance, has deduced that even if corpuscular properties are imputed to electromagnetic radiation [13], "Newton's radiation pressure is twice as large as Maxwell's for the same energy radiation" *i.e.* for energy incident at angle θ to the surface, Maxwell's pressure (horizontal component) is $F = (2\cos\theta/c)I$, whereas Newtonian mechanics yields $F = (4\cos\theta/c)I$, I being the kinetic energy flow incident on the surface. If $I = I(T)$, then one might expect temperature differentials to exist at equilibrium. The Boltzmann constant k' is inferred in statistical mechanics from systems in mechanical contact [14] in an ensemble, where the traditional supposition has been systems which statistically obey Newtonian dynamics with respect to momentum interchange, whereas for pure heat radiation, the momentum contact exchange between the surfaces (*i.e.* energy interactions) need not necessarily involve the same temperature parameter (with respect to Newtonian molecular momentum exchange) if the Planck inference is valid and if it can be derived *via* the principles of statistical mechanics.

Consider the system of standardized (meaning that the energy density is given by the Planck law with the associated constants) unit volume bb cavities that possesses exactly similar dipole oscillators in the boundary matrix (bm), and where [1] the temperature is T_c for both the bm and bb radiation. The bb radiation is defined to be at temperature T_c because it is in equilibrium with the bm, whose temperature may be determined by mechanical contact with a thermometer involving Newtonian corpuscular momentum transfer. We may suspend a body of known geometry and material composition in the cavity until it reaches radiathermal equilibrium (without Newtonian corpuscular momentum transfer in the Planck sense). We define the traditional statement of the Zeroth law to imply Newtonian corpuscular momentum transfer (with conservation) amongst the systems in contact and refer to this implication as ZLNM. We may replicate this system A times (where the bm's are contiguous and in thermal contact). By ZLNM, the bm's all have the temperature T_c. Since the suspended bodies are not in mechanical contact, we need not ascribe a Kelvin temperature T_c to it, although since they are exchanging energy with the bms, there must exist another parameter common to both, which must be determined. We suppose that the mean energy of a bm $\bar{E}_b$ and that of the suspended body $\bar{E}\,(N, V)$ obeys $\bar{E}_{bm} >> \bar{E}(N, V)$. Let $E_j\,(N, V)$ be a microstate of the suspended body (N being the number of particles say and V its volume). By the stationary entropy principle and Boltzmann's definition of entropy $S_A = k' \ln \Omega_A$, where Ω_A is the number of arrangements consonant with energy and mass conservation, it follows (for details of the standard methodology see ref. [14]) for the suspended body that the probability P_j of state j, $P_j = \exp[-\beta E_j(N,V)]/Q$, where the partition function is $\sum_j \exp[-\beta E_j(N,V)]$ and the average value $\bar{X}$ of thermodynamic variable X_j in state j is $\bar{X} = \sum X_j\, P_j$. We now consider two situations : *a'*) The bm's of each individual system denoted A without the smaller body C suspended in any of them, where the bm's now compose a canonical ensemble. *b'*) The ensemble as in *a'*) but with C suspended in each of the systems enclosed by the bm's. Since $\bar{E}_{bm} >> \dot{E}(N, V)$, each bm is a thermal reservoir [15] with respect to the C suspended within. For *a'*), each bm subsystem would [16] constitute a separate entity with ZLNM interaction and with temperature parameter β, the probability for energy state E'_j of a particular bm is $P'_j = \exp -\beta E'_j(N,V)/Q$. The connection between β and macroscopic thermodynamics is made by comparing (i) $(\partial\bar{E}/\partial V)_{N,\beta} + \beta(\partial\bar{P}/\partial\beta)_{N,V} = -\bar{P}$ with (ii) $(\partial E/\partial V)_{N,T} + T(\partial P/\partial T)_{N,V} = -P$, where P is the pressure, and the other symbols as previously defined. The ensemble postulate of Gibbs [14] relates directly any macroscopic thermodynamical variable X with ensemble average $\bar{X}$, *i.e.* $X = \bar{X}$ (with the exception of all global parameters such as β and μ, the chemical potential per particle). From (i) and (ii), it is inferred that $\beta = 1/kT$ for bm systems in *a'*), where k is a constant. By considering another system B in thermal ZLNM contact with A to form a system AB which is one member of like systems AB in an ensemble, it can be shown (assuming Ω_A and Ω_B are independent) that A and B [14] must have the same β; by inference from the Zeroth law in the ZLNM sense that the ***Kelvin*** temperature must be the same, then $k_A T = k_B T$ or $k_A = k_B = k$, where k is universal for ZLNM thermal equilibrium. Thus, the k value for the bm's (system A) is fixed and equal to the Boltzmann constant k'. For case *b'*), A and C are in radiathermal contact only. By repeating the derivation as for ZLNM contact, where in statistical mechanics the only assumptions for the canonical ensemble are : (1) energy and mass conservation and (2) independence of probability distributions of the microstates in systems A and C [14], we again derive that for systems A and C, β is same. But from (*a'*), $\beta = 1/kT_A$, hence

$$kT_A = k_C T_C, \tag{7}$$

where k is defined here to be Boltzmann's constant ($k = k'$) and subscripts refer to the system concerned; T is the Kelvin temperature for systems A and C depicted by subscripts respectively in eq. (6), and clearly T_A need not be equal to T_C ; k_C is defined as the radiathermal constant for body C in general, which is suspended inside the cavity of A, and is the analogue of the Boltzmann constant. However, k_C is specific to that particular body C. Suppose $C1$ also has a cavity in which $C2$ is suspended, where $C1$ was suspended in A (*i.e.* Chinese nested box arrangement), then

$$T_{C2}\, k_{C2} = k_{C1}\, T_{C1} = kT_A,$$

or

$$T_{C2} = (k.k/k_{C2}.k_{C1})T_A. \tag{8}$$

Suppose $C2$ is a bm for $C3$, $C3$ a bm for $C4$ and in general CN-1 is a bm for CN, then generalizing eq. (8) gives

$$T_{CN} = (k^n / \prod_{I=1} k_{CI})T_A. \tag{9}$$

The above is termed the series arrangement. The parallel arrangement is when "small" bodies $C_1, C_2, ...C_n$ are simultaneously suspended in cavity A, where $\sum \bar{E}_{C_i} <<< \bar{E}_A$, so that the radiation in the cavity A is determined by A only. Then if the systems C_1A, C_2A....... C_nA are all considered independent, the previous arguments would yield

$$kT_A = k_{C_i} T_{C_i} = k_{C_i} T_{C_i} \, (i = 1, 2, \ldots\ldots\ldots\ldots n) \tag{10}$$

Note that the C_i's and CI's in the parallel and series arrangement need not be equal for the same bodies and where $i = I$ from what has been stated. In general, for both arrangements, we might write (i capitalized and not subscripted or otherwise depending on the arrangement) $k_{C_i} = k_{C_i}(G,A)$, where G are all the variables pertaining to the body suspended in A (geometrical, thermodynamical, and compositional) and A are the variables for system A. There are 4 possibilities to consider : (i) k_{C_i} is a function of A and G, (ii) of G only, (iii) of A only, and (iv) of neither A nor G. Since surfaces in A and C causes the final results, there is no reason for preference ; only (i) or (iv) is anticipated. In (iv), we have $k_{C_i} = k_{C_j}$ for all i,j and a universal constant for thermal radiation equilibria results. Depending on the experimental outcomes, measurement standards based on fixed geometry and material variables may be specified for systems A and C. The relevant generalization for a standardized blackbody A not in ZLNM but in radiathermal equilibrium with a sample C_i inside it, where $E_{C_i} >> E_A$, can be written as [17]

$$P_e^{C_i}(-k, \alpha, \beta = T_{C_i} k_{C_i}) / a^{C_i}(k, \alpha, \beta) = P_i(k, \alpha, \beta) = f_A(\beta) \tag{11}$$

or

$$P_e^{C_i}(-k, \alpha, T_{C_i} k_{C_i}) / f_A(\beta) = \varepsilon_{C_i} = a^{C_i}(k, \alpha, \beta), \tag{12}$$

where $P_e^{C_i}$ is the emission in direction k, a^{C_i} the absorbance at the same temperature T_{C_i}, P_i the incident radiation of the standardized radiator A which is a function of $\beta = T_{C_i} k_{C_i} = \mathrm{kT}$ only, so that $P_i = f_A(\beta)$. The emissivity ε_{C_i} is defined with respect to A and no similar temperature is required *i.e.* $T_{C_i} \neq T = T_A$ in general. Hottel and Sarofim [7] have attempted to 'derive' a non-equilibrium Kirchoff law through the Ritchie experiment. We wish to state that the result here are anticipated only without any (for details of setup, see [7]) theoretical foundation ; for relative to some average temperature T_{ave}, we can write the heat transferred in unit time from the tinned side to the matted black surface *via* radiation by the function $R(T_s - T_b) = R(\Delta T)$, T_s and T_b being the respective temperatures of the tinned and matted black surfaces respectively, and where $R(0) = 0$. Then, by symmetry, $R(-\Delta T) = -R(\Delta T)$ if R is continuous at $\Delta T = 0$ since $R(\Delta T) = \partial R / \partial \Delta T | T_{ave} \Delta T +$........higher orders. Thus, we would not expect to first order, any significant difference in the heating rates to the two differential gas thermometers. The derivation of the generalized Kirchoff's laws are not based on a convenient geometry and symmetry of the system, as exists in the Ritchie experiment, and so the Hottel-Sarofim insertions are not correct.

3. Other thermodynamic consequences

3.1 Kelvin statement and entropy :

If a temperature difference exists between the bm of A and the suspended object C within, then there is the possibility of work extraction by a cyclical Carnot engine using the bodies as heat source and sink respectively, so there is net conversion of heat into work until the temperatures equalize which might occur at 0K. This might appear at first sight to violate principles that forbid perpetual motion machines of the Second kind. Thus, this phenomenon must be examined in the light of the statements of Clausius or Kelvin, which can be shown to be logically equivalent [18]. We examine Kelvin's Principle which states "It is impossible by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects". (A thorough discussion of this principle can be found in ref. [19]) Since in our system, both the boundary and suspended object cool down simultaneously, the one colder than the other, no contradiction to Kelvin's statement is found since when the temperatures equalize, no more work may be derived. However, Kelvin's Principle is relative to his system being composed of inert bodies with different temperatures, where the thermal heat transfer was assumed to be exclusively ZLNM type interactions. Hence, there would possibly be a further generalization of his system involving non-ZLNM interactions.

In fact, the entropy change in this situation is positive. Consider a system whose size does not adversely affect the temperature (as assumed for instance in the definition of the entropy increment $\delta Q/T$) when at unit time, increment of heat Q_2 absorbed at T_2 and ejected at temperature T_1 with heat increment Q_1 at the other boundary (assume $T_2>T_1$) ; the heat transported to the boundary at T_1 is dissipated back to the boundary at T_2 relatively instantly (for small systems where effects due to the velocity of light may be neglected) so that the entropy change is $\dot{S} = Q_1/T_2$. The work output $\dot{W}$ is $\dot{W} = (T_2-T_1)Q_2/T_2$ so that

$$\dot{S} = \dot{W}\{T_1/((T_2-T_1)T_2)\} \geq 0 \tag{13}$$

for the spontaneous process when $|\dot{W}| << \bar{E}_A, \bar{E}_{Cj}$, for any bm and suspended body respectively. The apparent movement of heat from a "mechanically" colder to hotter region about radiathermal equilibrium is due to the perturbation of the Carnot engine (from the point of view of radiathermal entropy, defined by $S' = dQ/\beta = dQ/(k_jT_j)$, where β is constant for both surfaces at radiathermal equilibrium, for any surface j with coupling constant k_j as discussed in the previous section. If there is an exchange of radiathermal (or other non – ZLNM) heat dQ between surfaces j and i at equilibrium, then $\delta S' = dQ(1/k_jT_j - 1/k_jT_i) = 0$ *i.e.* the variation of radiathermal entropy at equilibrium is zero since $\beta_j = \beta_i = k_jT_j = k_iT_i$ and the following implications become evident :

(1) At equilibrium, the variation of entropy is zero across regions with the same β parameter and follows from the above variation $dS' = 0$.

(2) There exists a general function of state S' with the non-ZLMN heat differential dQ, such that $dS' = dQ/(k(\boldsymbol{R})\,T) = dQ/\beta$ is the perfect differential, *i.e.*

$$\oint dS' = \oint dQ/k(\boldsymbol{R})T) = 0 \tag{14}$$

for all arbitrary transitions in thermodynamical space $\boldsymbol{R}$ where $k(\boldsymbol{R})$ is a local continuous coupling coefficient (with respect to variables $\boldsymbol{R}$) as discussed previously for discrete or separated surfaces k_j, where dQ is the heat differential which will be defined below. The space $\boldsymbol{R}$ may exist within the system as an ensemble of subsystems [20], or one that is deformed as is normally applied to the closed path in $\boldsymbol{R}$. The former is a generalization of the Second Law to steady state processes, and eq. (14) may thus also be generalized to these states where dQ_i is the net heat absorbed by the system due to heat vector $\boldsymbol{J}_{q_i}$ for energy form i, *i.e.*

$dQ_i = -\int_0^{\infty}\int_0^{\partial V} \Delta . \boldsymbol{J}_{q_i} \, dt \, dV$ during a slight perturbation of the system from one steady state to another, and ∂V is the system boundary for heat source and heat sink free regions. Equation (14) is a generalized version of the Second Law involving coupling function $k(\boldsymbol{R})$.

Proof of eq. (14) above

(a) Consider the elementary differential about equilibrium given above, *i.e.* (i) $dS' = dQ\,(1/k_jT_j - 1/k_iT_i) = 0$ for boundaries j and i. Then we can write $dQ'_j = dQ/k_j$ for all i,j such that (i) can be written as $dQ'_j/T_j - dQ'_i/T_i = 0$ which constitutes a virtual Carnot engine for an elementary cycle. Then, we can pave any arbitrary closed path for details of how this method is applied to derive the entropy differential in Thermostatics, see ref. [21]) by such virtual elementary cycles so that all heat exchange terms cancel internal to the boundary which is the closed path and eq. (14) results in exactly the same manner as the analysis of Carnot cycle pavings for a general cycle to derive the ZLNM entropy increment $dS' = \delta q / T$ as a perfect differential where $\delta q = dQ/k(\boldsymbol{R})$. Alternatively, the method of ensembles [14] may be used to show that $\beta = 1/k(\boldsymbol{R})T$ is an integrating factor to $\delta q_{rev} k(\boldsymbol{R}) = dQ = d\bar{E} - \sum_i P_j dE_j$, *i.e.* $\delta q_{rev}/T = dS'$ is a perfect differential.

If thermal energy has been injected into a system in radiathermal equilibrium, say at surface j, then it would heat up such that $\beta'_j > \beta'_{eq}$, where β'_{eq} was the original equilibrium radiathermal temperature. Thus, a flow of this heat from a 'hotter' to a 'colder' region is anticipated with increase in entropy, even if the term 'hotter' or 'colder' is reversed where Kelvin temperature T is considered because of the increase of entropy ΔS given by $\Delta S = -Q(1/\beta'_j - 1/\beta'_{eq}) \geq 0$ where -Q is the heat transported. Hence, even if $T_j < T_{eq}$, there can exist radiathermal transfer from surface j to a point at T_{eq} provided the variables satisfy $(k_{eq}/k_j) < 1, T_j \geq (k_{eq}/k_j)T_{eq}$.

The equations have been developed for classical systems in Euclidean space, and can be easily generalized in spaces where this geometry is not valid via differential forms [22] and tensors. From the above, if we define temperature in terms of the $\beta'(= k_jT)$ parameter, then for non-ZLMN form fo energy i which is transferred, we define "heat" for form i as that form of energy that traverses a boundary by virtue of a temperature difference $\Delta\beta'$, where the heat flux vector is denoted $\boldsymbol{J}_{q_i}$; this heat flux is defined to be the *conductive heat flux* for form i.

The above implies that the Fourier Principle as proposed by Benofy and Quay [23] regarding radiation transfer, cannot be correct (it may be termed correct for ZLNM type heat transfer only) and demands generalization. For conductive (ZLNM heat transfer, the principle states the $\boldsymbol{J}_q . \nabla T \leq 0$ always, where T is the Kelvin temperature and $\boldsymbol{J}_q$ the conductive heat transfer. We generalize this by stating that for pure conductive heat transfer via energy form i (non-ZLNM) in thermal equilibrium with distinctly different energy form j (also non-ZLNM) and form due to ZLNM processes with ***conductive*** (as opposed to other types of energy transfer [23]) heat vector $\boldsymbol{J}_q$, we have each of the following holding simultaneously and separately ; $\{\boldsymbol{J}_{qi} . \nabla\beta_i \leq 0, \boldsymbol{J}_{qi} . \nabla\beta_j \leq 0$ and $\boldsymbol{J}_q . \nabla T \leq 0\}$, where $\beta_i(\boldsymbol{R}) = k_iT_i$ for all i, and k_i is a function of geometry and thermodynamical variables $\boldsymbol{R}$ and is the coupling constant discussed previously in the section on ensemble theory. For discrete surfaces, clearly k_i is a global coupling factor, so that the gradient $\nabla\beta_i$ is replaced by $\nabla\beta_i = \beta_{S_{1i}} - \beta_{S_{2i}}$ (when the region between the surfaces is not a source of energy form i) for transfer between surfaces S_1 and S_2. Clearly, the conventional definition of heat in thermodynamics is then equivalent to conductive heat as defined here (for further details see reference [23]) for ZLNM type interactions. By definition of our generalized conductive heat, assuming continuous behaviour of the variables and heat transfer rates, the rate of heat transfer would be a function of the temperature difference per unit length, so that first order fourier-like equations for conductive heat for each of the different energy forms i and j is envisaged, and may be written for each i as follows

$$\boldsymbol{J}_{qi} = -\boldsymbol{K}_i : \nabla\beta_i \tag{15}$$

where K_i is the conductivity tensor and $\nabla\beta_i$ the generalized temperature gradient, where $\nabla\beta_i = \nabla k_i T_i$. We have demonstrated that eq. (15) is true for radiation experimentally, and this therefore further subjects to question attempts to use previously developed potentials [24] for a bb T^4 Power Law [24, 25]. Eq. (15) may be generalized to any order. The conductive heat transfer $dQ_i = \nabla . \boldsymbol{J}_{q_i}\ dt$ is written in classical notation for Euclidean spaces as stated before. We have to modify these for systems of a different metric to the appropriate "divergence" *via* differential forms, *e.g.* $\int_M d\omega = \int_{\partial M} \omega$ where $d\omega = \operatorname{div} \boldsymbol{J}_{q_i}$ and ω is the appropriate 1-form [22–26]. This work has stressed on the coupling due to electromagnetic waves but the above terminology "energy form" may refer to all other non-ZLNM processes, including possibly gravitational heat and gravitational thermal waves as well.

3.2. General equilibrium criterion and consequences :

We consider here scalar quantities which can easily be generalized via tensors. Consider two systems at (say) two very different pressures and particle densities which are brought together to share a common diathermal wall dW. Then, for each system, the total impulse $\boldsymbol{F}dt$ delivered to the wall is $dt \int_{dw} P_p d\boldsymbol{A}$ which must be balanced (P_p being the average pressure component of the system, S the surface area and $\boldsymbol{A}$ vector area) by an equal and opposite impulse dt. $\boldsymbol{T} = dt \int_{S-dw} P_p d\boldsymbol{A}$ over the entire boundary surface other than dW, where $\boldsymbol{T}$ is termed the tension (and is not necessarily the same for each system). At the interface dW, the probability of simultaneous collisions between molecules of one system with the other mediated by the wall is small. Consider an average particle momentum (+ve) $p1$ of the less dense system colliding via dW with a particle of the more dense system with average momentum $p2$ (-ve) with linear momentum conservation, where we consider only the normal component to the surface. Let $|p1| > |p2|$, with primed variables for the momentum after collision. Then $|p2'| > |p2|$, and with randomization, a net transfer of thermal energy would take place. We therefore, define the net zero current equilibrium state to be one where the *mean momentum change per particle* or *complexed quantum* [26] within the systems to be zero for all interactions. In the quantum theory, Einstein [27] heuristically connected the thermalized e.m. radiation to that of material particles from the analogy of the entropy expression for particles and monochromatic (thermal) radiation, where all frequency modes are independent. Thus, the above criterion if coupled with the Einstein analogy and extended to thermalized e.m. waves would imply through the De Broglie relations for two bbs connected through a radiation channel that $(\langle h(T_1)\rangle \nu - \langle h(T_2)\rangle \nu)/c = 0$ or $\langle h_{m_1}(T_1)\rangle = \langle h_{m_2}(T_2)\rangle$ for two materials m_1 and m_2 in radiathermal equilibrium where $\langle h_m(T)\rangle$ is the bb Planck constant for material m as determined at temperature T, which is almost not feasible since these constants are measured at very high temperatures. The other alternative which is not theoretically nor experimentally equivalent, is through photoelectric effect measurements. Thus, a very mild variation in the material "Planck" constant is anticipated from Zon's (*op cit*) hypothesis at fixed temperatures (at either T_1 or T_2 where $T_1 \neq T_2$ at radiathermal or non-ZLNM equilibrium) for each of the materials m_1 and m_2 (where equality holds when m_1 is at T_1 and m_2 at T_2).

The Planck constant as determined in early blackbody or photoelectric studies [28] shows marked variations (*e.g.* h = 4.2 to 5.2 for Richardson and Compton's work [28]) and Millikan's work gives 6.57 ± .5% which corroborates Westphal's results nearly exactly but is not within tolerance of current quotations given his .5% error estimate. Millikan used other corrective factors like the metallic contact e.m.f. involving the Planck constant [28], the very constant he was determining and only very few certain fixed frequencies which lead to corroboration with other estimates in his time (which were presumably incorporated in the work function in other measurements by other workers where ambiguous and large divergence is reported by Millikan). A discussion of the results of the Compton and Richardson 1912 experiments is given in ref. [29] and J. J. Thompson's verdict of the experiments up to 1914 in ref. [30]). The straight line graph passes nearly perfectly through all the frequency coordinates chosen in Millikan's experiments, implying a belief of an absolute Quantum of action represented by the Planck constant. From the recent work [1], the Planck constant is a total system property that involves averaging, $h\nu$ being the *average* energy transfer for all the frequency modes, and need not hold exactly for each mode and therefore *does allow for the scattering of values* as reported by all other workers. Advanced Undergraduate experiments reveal [31] a large scatter (~10–20% being the typical reported values) of points about the linear prediction of stopping voltage and frequency in spite of instruments of arguably much lower tolerance and much higher accuracy than that used by Milliken. It would thus appear that the Planck constant is defined precisely, and standardized as such by spectroscopic determination of the emission lines of atoms such as Hydrogen, whose values are close to those determined by photoelectric and bb emission studies, rather than directly from the latter. If the density distribution for mean photon numbers is considered valid (where $\bar{n}_s = 1/(\exp \beta\varepsilon_s - 1)$) and given the radiathermal *equilibrium* temperatures of two cavities 1 and 2 respectively at temperatures T_1 and T_2, then equilibration of photon species for each of these cavities implies

$$\langle h_1\rangle/kT_1 = \langle h_2\rangle/kT_2$$

or

$$\langle h_1\rangle/\langle h_2\rangle = T_1/T_2\,,\ \text{if } k_1 = k_2 = k. \tag{16}$$

Relative to cavity 1, let the radiathermal coupling constant be k_{12}, where system 1 has been parametrized according to the Zeroth Law. Then since $kT_1 = k_{12}T_2$, we have

$$\langle h_1\rangle/\langle h_2\rangle = (k_{12}/k) \tag{17}$$

(for the above case (eq. (16)) or $\langle h_1\rangle/\langle h_2\rangle = 1$

for the relationship between the apparent change of the Planck constant with the ZLNM thermal coupling constant k (Boltzmann's constant). If $T_1 = 300$K, and the temperature variation 1 K, then the variation of h is a low .33%. Eqs. (12–13) are based on the validity of the density function and relative to the present approach can only be an approximation.

4. Summary and Conclusion

1) It is possible to reconcile from classical Brownian motion considerations the experimental outcome of a linear term in temperature of the radiant heat flux, and that the physical dimensionality of the system must be considered in determining whether bb radiative flux is the principle form of heat transfer or not.
2) Considerations concerning the density of state and the nature of the Planck quantum in terms of the relaxation time of all the surface oscillators of a bb cavity lead to another form of the radiancy expression in the presence of a medium with refractive index other than unity.
3) From Zon's suggestion [12], that it is theoretically feasible to contemplate a divergence of the bb Planck temperature and the oscillator Maxwellian temperature, where the earlier work [1] parametrized the Planck temperature in accordance with generalized equipartition over the whole set of oscillators with a common relaxation time, we attempted to reconcile the classical algebraic demands of ensemble theory with the predicted (and experimentally verifiable – as our experiments suggests) possibility of minute temperature differences at "equilibrium", resulting in the extensions of the Zeroth, Kirchoff, Second and Fourier Laws [23]. The predicted radiathermal constant would be 'universal' if it is independent of geometry and temperature. This analysis can be extended to other forms of energy interactions resulting in the same structure of coupling constants k_{ij} deduced here for radiation (other possibilities include thermal gravity waves, *e.g.* that which is predicted to be propagated in massive body collisions and other energy interactions arising from the independent forces predicted in particle theory).

Some other important considerations not developed here are the possible dependence of the above mentioned fundamental constants on geometry and magnitude of the system.

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Appendix

Nomenclature

- a' general electromagnetic viscosity
- a Kirchhoff absorptivity
- A Averaging coefficient due to blackbody radiation in surface microcavities
- c velocity of light
- $D(\nu)$ density of cavity radiation
- D_i i-th channel process partition function
- e electric charge
- E energy density
- $\boldsymbol{E},\boldsymbol{E}'$ electric field vectors of propagating electromagnetic wave
- $E_{h\nu}$ radiancy of Planck blackbody spectrum
- g geometric factor variables, equation (5)
- h Planck constant

$\boldsymbol{J}_q$	heat current vector
k''	elastic constant of surface oscillator
k'	Boltzmanns (thermal) coupling constant
k_s	thermal coupling factor for any system
$\boldsymbol{K}$	conductivity tensor
l_i	the i-th power coefficient in temperature for surface oscillator leakage current
m	mass of oscillator
n	complex index of refraction
n''	charge density
$\boldsymbol{n}$	unit normal from the surface
N	number of scatterers or oscillators
$p(E)$	probability density function for energy E
$\boldsymbol{P}$	polarization
P	average radiant energy emitted per oscillator
P_e	Kirchhoff emission power
P_K	total radiathermal emission
P_i	incidence power on a surface
Pp	average pressure of the system
Q	heat content variable
S	entropy function
T	Kelvin temperature
T_M	Maxwellian temperature
T_P	blackbody temperature
$\boldsymbol{T}$	tension in the system
u	unit normal of wave vector
u_o	field energy density
U_ν	Planck energy density (per unit frequency and per unit volume)
X	oscillator amplitude
$X_{..}$	maximum oscillator amplitude

Greek symbols

α	$= m\langle X_0^2\rangle/2$
α'	$= e^2\pi/hc$
γ	= viscosity damping term
β	general temperature factor
Π	blackbody permeability factor
ν	oscillator frequency
τ	mean system relaxation time
ω	oscillator angular frequency